<Division of Synthetic Chemistry>Organoelement Chemistry

Division of Synthetic Chemistry
– Organoelement Chemistry –

http://boc.kuicr.kyoto-u.ac.jp/www/index-e.html

Prof
TOKITOH, Norihiro
(D Sc)

Assoc Prof
SASAMORI, Takahiro
(D Sc)

Assist Prof
MIZUHATA, Yoshiyuki
(D Sc)

Assist Prof
AGOU, Tomohiro
(D Sc)

Techn Staff
HIRANO, Toshiko

PD
GUO, Jing-Dong
(Ph D)

PD
MAJHI, Paresh Kumar
(Ph D)

Students

MIYAMOTO, Hisashi (D3)
NAGATA, Koichi (D3)
AWANE, Hiroyuki (D2)
HIRANO, Koki (D2)
SUZUKI, Yuko (D1)
FUJIMORI, Shiori (M2)
SUGAHARA, Tomohiro (M2)
HONJO, Kazuma (M1)
NAKANO, Tomohiro (M1)
YANAGISAWA, Tatsuya (M1)

Guest Scholars

KYRI, Andreas — University of Bonn, Germany, 30 April-31 August
FAßBENDER, Jan — University of Bonn, Germany, 23 August-4 September

Guest Res Assoc

STREUBEL, Rainer — University of Bonn, Germany, 6 June-11 June
MAYER, Ulrich F. J. — Mayer Scientific Editing, Germany, 19 May-13 June

Scope of Research

Organic chemistry has mainly developed with the use of second-row elements such as carbon, oxygen, and nitrogen, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds has been a dream for organic chemists. Our main research interest is the elucidation of the similarities and differences in structures and reactivities between organic compounds and the corresponding heavier congeners. These studies are interesting and important from the standpoints of fundamental chemistry, and open the way to more extensive application of main group chemistry.

KEYWORDS

Steric Protection
Kinetic Stabilization
Low-coordinated Species
Heteroatom
Transition Metal Complexes

Selected Publications

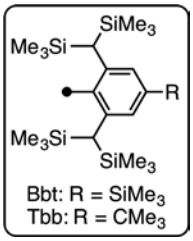
Sasamori, T.; Sugahara, T.; Agou, T.; Sugamata, K.; Guo, J.-D.; Nagase, S.; Tokitoh, N., Reaction of a Diaryldigermyne with Ethylene, *Chem. Sci.*, **6,** 5526-5530 (2015).

Agou, T.; Wasano, T.; Sasamori, T.; Guo, J.-D.; Nagase, S.; Tokitoh, N., Ring Expansion to 1-Bromo-1-alumacyclonona-2,4,6,8-tetraene by Insertion of Two Alkyne Molecules into the Al–C Bonds, *Angew. Chem. Int. Ed.*, **54,** 9568-9571 (2015).

Sasamori, T.; Sugahara, T.; Agou, T.; Guo, J.-D.; Nagase, S.; Streubel, R.; Tokitoh, N., Synthesis and Characterization of a 1,2-Digermabenzene, *Organometallics*, **34,** 2106-2109 (2015).

Reactions of Diaryldigermynes with Ethylene and Acetylene

Recently, divalent or multiple-bonded compounds of heavier group 14 elements have received much attention as potential transition metal–free catalysts. We have investigated the reactivity of stable Ge–Ge triple-bond compounds, digermynes, with small molecules and reported their unique and transition metal–free transformations with ethylene and acetylene.



Reaction of the digermyne BbtGe≡GeBbt (**1a**, Bbt = 2,6-[$CH(SiMe_3)_2$]$_2$-4-[$C(SiMe_3)_3$]-C_6H_2) with ethylene initially afforded the corresponding 1,2-digermacyclobutene **2**. Depending on the reaction conditions applied, further reaction of **2** with ethylene furnished two different reaction products: 1,4-digermabicyclo[2.2.0]hexane **3** or a bis(germiranyl)ethane **4**. Combined experimental and theoretical results suggested that **3** and **4** are the thermodynamic and kinetic reaction products, respectively.

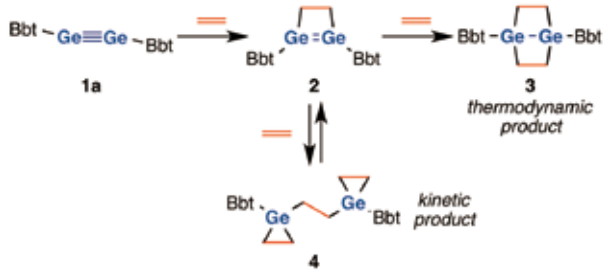


Figure 1. Reactions of digermyne **1a** with ethylene.

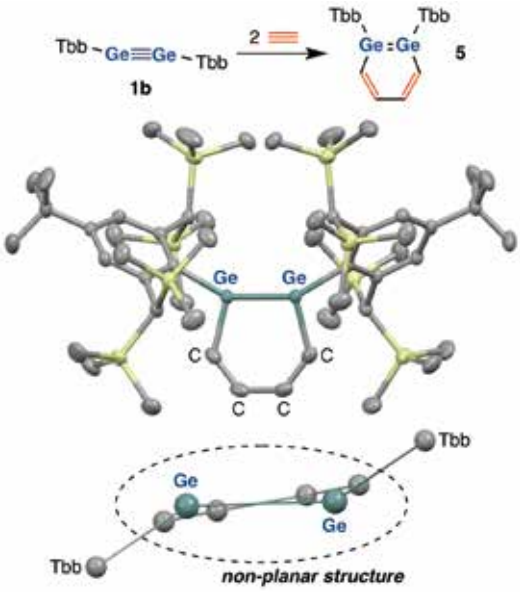


Figure 2. Reaction of digermyne **1b** with acetylene and the structure of **5** (overhead and side views).

The reaction of the digermyne TbbGe≡GeTbb (**1b**, Tbb = 4-*t*-Bu-2,6-[$CH(SiMe_3)_2$]$_2$-C_6H_2) with two equivalents of acetylene gave the 1,2-digermabenzene **5** as a stable, crystalline compound via a formal [2 + 2 + 2] reaction. The [Ge_2C_4] ring of **5** exhibited a nonplanar structure, wherein six π electrons are partially delocalized. Despite its non-planar structure, theoretical calculations suggested aromaticity for **5**, comparable to that of 1,2-disilabenzenes.

Formation of an Alumacyclononatetraene by Insertion of Two Alkyne Molecules into the Al–C Bonds of an Alumacyclopentadiene

The reaction of heteroles with compounds containing carbon–carbon multiple bonds, such as alkynes, is a useful method to construct new heterocyclic skeletons with specific structures and properties. Treatment of 1-bromo-2,3,4,5-tetraethylalumole (**6**) with 3-hexyne afforded the corresponding ring-expansion product 1-bromo-1-alumacyclonona-2,4,6,8-tetraene (**7**), accompanied by the formation of hexaethylbenzene. Compound **6** is, to our knowledge, the first example of structurally characterized, stable group 13 element–containing cyclononatetraene derivative. The AlC_8 nine-membered ring of **6** exhibited a highly twisted, nearly C_2-symmetric structure both in the crystalline state and in solution. Deuterium-labeling experiments and DFT calculations on the reaction of **6** with 3-hexyne suggested that 1-bromo-1-alumacyclohepta-2,4,6-triene (**8**), which is formed by the insertion of one molecule of 1-hexyne into the Al–C bond of alumole **6**, is the key intermediate for the generation of **7** as well as hexaethylbenzene.

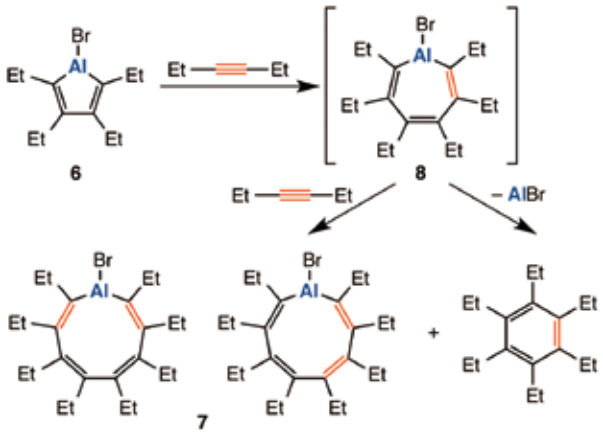


Figure 3. Reaction of bromoalumole **6** with 3-hexyne.